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(21) International Application Number: PCT/GB00/01652 (22) International Filing Date: 28 April 2000 (28.04.00) (30) Priority Data: 99303444.6 30 April 1999 (30.04.99) EP (71) Applicant (for all designated States except US): ALCAN INTERNATIONAL LIMITED [CA/CA]; 1188 Sherbrooke Street West, Montreal, Quebec H3A 3G2 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): BROWN, Stephen, Clifford [GB/GB]; 37 Thompson Drive, Caversfield, Bicester, Oxfordshire OX6 9FA (GB). DAVID, Marie-Laure [FR/FR]; Résidence Les Amandiers, Appartement 75, 17, rue Winston Churchill, F-60200 Campiegné (FR). EVANS, Kenneth, Arthur [GB/GB]; Westward View, 4 Hillford Road, Chalfont St. Peter, Buckinghamshire SL9 0DX (GB). GARCIA, Javier, Prieto [ES/GB]; 47 Coopers Gate, Banbury, Oxfordshire OX16 2EQ (GB). (74) Agent: EASTWOOD, Simon, Christopher; Stevens, Hewlett & Perkins, 1 St. Augustine's Place, Bristol BS1 4UD (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FIRE RETARDANT COMPOSITIONS (57) Abstract <p>A polymer composition is provided that comprises a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler. The second filler may be a material with known flame retardant properties, an inert filler or a combination of the same. The preferred nano-clay is Cloisite, the preferred second filler is aluminium trihydroxide. The presence of this flame retardant additive combination in polymers increases the strength of the char that forms during combustion. The formation of a strong char creates a barrier to ignition of the underlying material, for example electrical cables that have been provided with a coating of the polymeric composition.</p>		

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FIRE RETARDANT COMPOSITIONS

This invention relates to fire retardant or flame retardant (these terms being synonymous for present purposes) additives for polymeric materials. More particularly, it relates to such additive compositions which have the effect of increasing the strength of the char formed when plastics burn.

The combustion of a polymer leads to the formation of a carbonaceous residue, ash or char. Many fire tests, such as the single burning item (SBI), UL94 and 3m-cube test (IEC1034 - also mentioned in other standards, for example BS 6724:1990 appendix F), have shown the importance of the physical properties of this char in controlling the flammability of plastics. Foamy char structure appears to be more fire resistant than brittle, thin char. Additives that increase the amount of char formation are known to be effective fire retardants. Fire-retardant additives for Polymeric Materials – I. Char Formation from Silica Gel-Potassium Carbonate, J W Gilman *et al* , Fire and Materials, Vol 21, 23-32 (1997) contains a review of char formation in various plastics and reports on the effect that silica gel and potassium carbonate additives have on polymer flammability.

When a plastic cable burns, the slumping or dripping of flaming polymer promotes the progression of the fire. The formation of a stable char layer after combustion of a section of the cable may protect the underlying part of the cable structure as it creates a barrier to further ignition. Furthermore, the formation of a char layer is believed to be responsible for the reduction in the rate of heat release sometimes observed in the Cone Calorimeter. Additives which have the effect of increasing the strength of the char formed when a plastic coated cable burns are therefore extremely valuable.

Nano-composites, made by mixing two or more phases such as particles, layers or fibres, where at least one of the phases is in the nanometre size range, are well known. Nano-clays and nano-composite clays are also known.

WO 97/30950 describes the manufacture of one type of such clays from smectite, in particular montmorillonite, and its use in thermoplastics. A family

of such nano-clays is sold under the trade mark Cloisite. These are the reaction product of a smectite-type clay and a mixture of a quaternary ammonium compound and a chain transfer agent. The table below gives the organic modifiers that are used for the different grades of Cloisite. The clays are said to be useful as additives or fillers for polymers. Each grade is adapted to use in a particular type of polymer. The resulting polymer composites can be moulded into articles by conventional shaping processes, such as injection moulding and extruding, so as to form for example components for the electrical and electronics industries. Among the properties noted for the polymer composites are improved ignition resistance and non-drip characteristics.

	Organic Modifier (1)	Modifier Concentration	% Moisture	% Weight Loss on Ignition
Cloisite® 6A	2M2HT	140 meq/100g	2%	47%
Cloisite® 15A	2M2HT	125 meq/100g	2%	43%
Cloisite® 20A	2M2HT	95 meq/100g	2%	38%
Cloisite® 10A	2MBHT	125 meq/100g	2%	39%
Cloisite® 25A	2MHTL8	95 meq/100g	2%	34%
Cloisite® 30A	MT2EtOH	95 meq/100g	2%	32%
Cloisite® Na ⁺	(natural sodium montmorillonite)		4%	7%

- (1) 2M2HT: dimethyl dihydrogenated tallow ammonium
 2MBHT: dimethyl benzyl hydrogenated tallow ammonium
 2MHTL8: dimethyl hydrogenated tallow 2-ethylhexyl ammonium
 MT2EtOH: methyl tallow bis-2hydroxy ethyl ammonium

Nanocomposites: Radiative Gasification and Vinyl Polymer Flammability,

J W Gilman *et al* , International Wire and Cable Symposium Proceedings 1997, 761-774 contains a report that nylon-6 clay-nano-composites have improved char characteristics compared to pure nylon-6. There is also teaching to add clays to other polymers such as polystyrene and polypropylene-based polymers.

Fire Retardant Polyetherimide Nanocomposites, Jongdoo Lee *et al* , Mat. Res. Soc. Symp. Proc. Vol. 457, 1997 Materials Research Society, 513-518 reports the improved char formation brought about by the addition of nano-composites to plastics.

US Patent No 5,342,874 describes halogenated polymer formulations having flame retardant properties. They contain a synergistic flame retardant combination consisting of an aluminium or magnesium hydroxide and a tetravalent tin compound.

With the use of polymeric materials still on the increase, there is a need for improved fire retardant additives. The present invention is based on the finding that a combination of two or more previously known fire retardant additives gives a surprisingly strong effect.

According to this invention there is provided a polymer composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler, wherein, during combustion of the composition, a coherent char is formed.

A coherent char is a char which holds together and would not fall off an underside surface when that surface is positioned substantially horizontally.

It has been found that the presence of this flame retardant additive combination in polymers greatly increases the strength of the char that forms during combustion. As explained above, the formation of a strong char creates a barrier to ignition of the underlying material. The compositions of this invention are flame retardant at least in part because a strong char is formed.

The polymer composition of this invention may contain any nano-clay. However, Cloisite nano-clays (manufactured by Southern Clay Products, Inc) are particularly preferred.

With regard to the second filler, this could be a known flame retardant such as aluminium trihydroxide (ATH) or an inert filler such as chalk or talc or glass powder. ATH is particularly preferred. An inert filler is one that does not have a flame retardant effect when used alone in a polymer. Other known inert fillers or flame retardant fillers could be used instead of or in addition to those listed above and still produce a synergistic effect. Examples of these include: magnesium carbonate, magnesium hydroxide (which could be added as either the refined compound or the ore Brucite), hydromagnesite, Huntite, boehmite, bauxite, borates (e.g., zinc borates) and molybdates (e.g., ammonium molybdates) particularly in combination with ATH and the nano-clay. It is to be understood that these fillers may be added to the nano-clay containing composition either individually or in combinations of two or more.

The particle size of the second filler is preferably less than $10\mu\text{m}$, more preferably less than $5\mu\text{m}$, most preferably less than $2\mu\text{m}$. The second filler may have a surface area which is greater than $1\text{m}^2/\text{g}$, preferably not greater than $35\text{m}^2/\text{g}$.

The proportion of the nano-clay component to the other filler component in the compositions of this invention is typically from 90% : 10% to 10% : 90% by weight. The proportion of nano-clay is preferably between 1 and 20% by weight of the total filler content. The total filler content (i.e. nano-clay plus the other filler) is from 20% to 80%, preferably from 40% to 70% by weight. The compositions may also include further constituents which are routinely present in conventional fire retardant products, such as stabilisers.

According to a further aspect of the present invention, there is provided a polymer composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler comprising at least one of aluminium trihydroxide, magnesium carbonate, magnesium hydroxide (or the ore Brucite), hydromagnesite, Huntite, boehmite and bauxite.

According to a further aspect of the present invention, there is provided a polymer composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler

comprising at least one of chalk, talc and glass powder.

The fire retardant additive combinations which characterise this invention are suitable for inclusion in a wide range of plastics. Examples of suitable polymers include polyamides, nylons, polyesters, epoxy resins, ABS combinations, halogenated polymers such as polyvinyl chloride (PVC), polyethylenes, polypropylenes, polyurethanes, polystyrenes, polychloroprene, phenolics, silicones, and silicone rubbers and copolymers and combinations of polymers. The particularly preferred use of the compositions of this invention is in cables for electrical or optical transmission. Flexible PVC has been a material of choice for cable sheathing for many years. The compositions may, for example, also be used to coat other moulded or extruded materials. The coating may be, for example, a sheath, jacket or insulation.

According to a further aspect of the present invention, there is provided the use of the polymer composition as a char promoter.

There is also provided a char promoting composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler.

According to a further aspect of the present invention, there is provided a method of improving the char promoting properties of a polymer composition, which method comprises the steps of combining a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler.

The compositions of this invention result from the finding that adding a nano-clay, such as Cloisite, and a second filler, such as ATH, to plastics surprisingly and significantly increases the strength of the char that forms during combustion. The reason for this synergistic effect is not known. It is possible that the ATH or other filler aids mixing of the clay and the polymer, or perhaps there is some chemical or physical effect that occurs during burning, or perhaps the fillers mechanically reinforce the char, or the filler acts as a support for the nanoclay, but the applicant is not restricted to these explanations.

The synergistic effect is illustrated in the following example. Of the three sample formulations tested (namely: one with ATH alone, one with nano-clay alone and one with both of these additives), only the sample of the composition according to this invention was able to pass the char test.

5 The invention will now be described, by way of illustration, with reference to the following examples and in which:

Figures 1 and 2 show silica mapping of Example 1; and

Figures 3 to 6 show char test results for Example 2.

10 **EXAMPLE 1**

Formulations:

The following three formulations were prepared according to the procedure described below.

EVA45 is based on 65% ATH, EVA46 on 5% nano-clay, and EVA47 on
15 60% ATH plus 5% nano-clay. All percentages are by weight.

Ingredients	EVA045-99	EVA046-99	EVA047-99
Escorene Ultra 00119 (EVA)	100	100	100
SF7E (ATH)	185	-	170
Cloisite 30A	-	5.3	15
Aminosilane 1100 (coating for ATH)	1.85	-	1.7
Irganox 10-10 (stabiliser)	0.5	0.5	0.5

The figures quoted in the table are "phr", i.e. parts by weight per hundred parts of polymer. In the table, the compositions are given in parts by weight.

Procedure:Mixing

EVA45 and EVA47 were produced on a Banbury BR1600 (batch mixer) according to the following procedure. The ingredients were added in the following order:

1st addition: Escorene + half of the filler.

2nd addition: half of the filler + silane + stabiliser (+ nano-clay for EVA47).

They were mixed until the ingredients were adequately dispersed.

A different recipe was used to mix EVA46. Namely, the three ingredients were placed together and mixed until an adequate dispersion was obtained.

The batches from the Banbury mixer were then calendered on the two roll mill at approximately 95°C to form a hide. 3mm thick by 15cm square plaques were compression moulded at 150°C from the hide and 5cm square samples were cut out from the plaques and tested according to the char test procedure (described below).

A plaque of each of the compounds EVA46 and EVA47 was frozen using liquid nitrogen, and broken into 2 pieces. The fractured surface was then analysed using EDS mapping. Aluminium and silicon enriched areas were mapped to determine whether the nano-clay was well dispersed.

Char Test Procedure

The samples to be subjected to the test are in the form of panels measuring 5 cm² and 3 mm in thickness. They are held vertically by means of a U-shaped frame. A load cell incorporated in the frame is connected to a chart recorder.

Once the apparatus has been set up, a fish tail flame is applied to the bottom edge of the panel. The flame impinges along the whole length of the bottom edge of the panel in the frame. It is allowed to burn and the mass of the panel diminishes. The chart recorder plots mass loss against time.

The test continues until either there is no more mass loss or there is a sudden mass loss. If the sample under test has formed a strong char which is staying in place (this is an example of a coherent char), the mass loss curve

will be asymptotic to time. At the end of the test, the sample either falls out of the frame or stays in the frame. In the latter case, the sample panel can be tapped and if it still remains in the frame then a strong char has been formed during its combustion.

5 The tapping test was carried out on samples subjected to the char test that did not show substantial sudden weight loss during the test. Although subjective, it provides a good indication of how coherent the char is. The test is performed by tapping the char with a metal spatula. Char that disintegrates or falls off easily is rated 1 or 2. Char requiring a harder tap to cause it to
10 break off was rated 3 or 4 and deemed to have passed the test. The most coherent char that survived tapping was rated 5.

Results:

Both EVA45 and EVA46 failed the test and fell from the sample holder in
15 about one minute. EVA47 stayed on the sample holder for the whole duration of the test. It gave a total mass loss of 49% and a strong char.

The nano-clay is mainly constituted of silica. Therefore, silica was mapped on both EVA46 and EVA47. The results are shown in Figures 1 and 2 (the silicon clusters, representing clay, appear as white dots). EVA46
20 showed large agglomerates of clay (up to 100 μm). Clay particles up to 10 μm were still visible in EVA47.

Neither ATH nor nano-clay gave a strong enough char when used on their own at the conventionally recommended addition levels. The results demonstrate that the only way to obtain a strong char is to use both together.

25 Very coarse agglomerates of clay were observed in EVA46. Agglomerates were still visible in EVA47 but were much smaller. The ATH seems to have helped the dispersion or mixing of the clay. This could explain the results obtained during the char test. However, it is not clear if this is the only explanation for the strength of the char.

EXAMPLE 2**Formulations:**

The following formulations were prepared according to the procedure described below.

- 5 EVA119 and EVA121 are based on 65% filler, EVA120 and EVA122 60% filler plus 5% nano-clay. All percentages are by weight.

Ingredients	EVA119	EVA120	EVA121	EVA122
Escorene Ultra 00119	100	100	100	100
Polcarb	185	170	-	-
Ultracarb 5	-	-	185	170
Cloisite 30A	-	15	-	15
Irganox 10-10	0.5	0.5	0.5	0.5

In the table, the compositions are given in parts by weight.

- 10 Polcarb is a 1-micron CaCO_3 with a surface area of $7\text{m}^2/\text{g}$ sold by ECC.
 Ultracarb 5 is a mix of huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) and hydromagnesite ($\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), with a d_{50} lower than 1 micron and a surface area of $15\text{m}^2/\text{g}$, that is sold by Microfine Minerals.
 Cloisite 30A is a nanoclay sold by South Clay Products and which has
 15 been treated using a surface modifier specially chosen for EVA polymers.

Procedure:

EVA119, 120, 121 and 122 were produced on the Banbury BR1600 according to the following procedure:

- 20 1st addition: Escorene + half of the filler (+ nanoclay for EVA120 and EVA122) then mix.

2nd addition: half of the filler + stabiliser then mix and afterwards cool for 2 minutes at 10RPM.

5cm square samples were prepared and tested in the char test as

described in Example 1.

Results (see Figure 3 to 6):

Char test/LOI

- 5 Both EVA119 and EVA121 failed the char test in one to two minutes. EVA120 and EVA122 passed the test. They gave a char strength respectively 3 and 4.

	EVA119	EVA120	EVA121	EVA122
Max Total Mass Loss by Char Test	-	40.5%	-	62%

- 10 It can be seen that both fillers alone failed the char test, but passed in the presence of the nanoclay. The filler alone does not give any char. The clay alone is dragged down from the sample support by the melting polymer before acting as a char promoter.

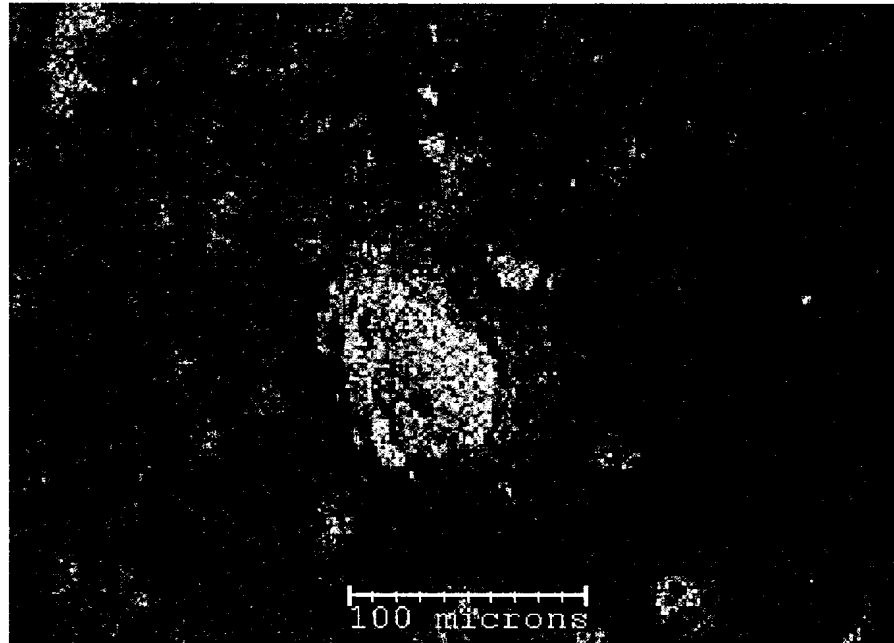
CLAIMS

1. A polymer composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler, wherein, during combustion of the composition, a coherent char is formed.
2. A polymer composition as claimed in claim 1, wherein the nano-clay is Cloisite.
3. A polymer composition as claimed in claim 1 or claim 2, wherein the second filler is a known flame retardant filler, an inert filler or a combination thereof.
4. A polymer composition as claimed in any one of claims 1 to 3, wherein the second filler comprises at least one of aluminium trihydroxide, magnesium carbonate, magnesium hydroxide (or the ore Brucite), hydromagnesite, Huntite, boehmite and bauxite.
5. A polymer composition as claimed in any one of claims 1 to 3, wherein the second filler comprises at least one of chalk, talc and glass powder.
6. A polymer composition as claimed in any one of claims 1 to 5, wherein the proportion of the nano-clay to the second filler is from 90% : 10% to 10% : 90% by weight.
7. A polymer composition as claimed in any one of the preceding claims, wherein the total filler content is from 20% to 80% by weight.
8. A polymer composition as claimed in any one of the preceding claims, wherein the polymer is PVC.

9. A polymer composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler comprising at least one of aluminium trihydroxide, magnesium carbonate, magnesium hydroxide (or the ore Brucite), hydromagnesite, Huntite, boehmite and bauxite.
10. A polymer composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler comprising at least one of chalk, talc and glass powder.
11. A cable or wire coating formed from a polymer composition according to any one of claims 1 to 10.
12. A moulded or extruded material coated with a polymer composition according to any one of claims 1 to 10.
13. Use of a polymer composition according to any one of claims 1 to 10 as a char promoter.
14. A char promoting composition comprising a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler.
15. A method of improving the char promoting properties of a polymer composition, which method comprises the steps of combining a polymer and a synergistic flame retardant additive combination which comprises a nano-clay and a second filler.

1 / 3

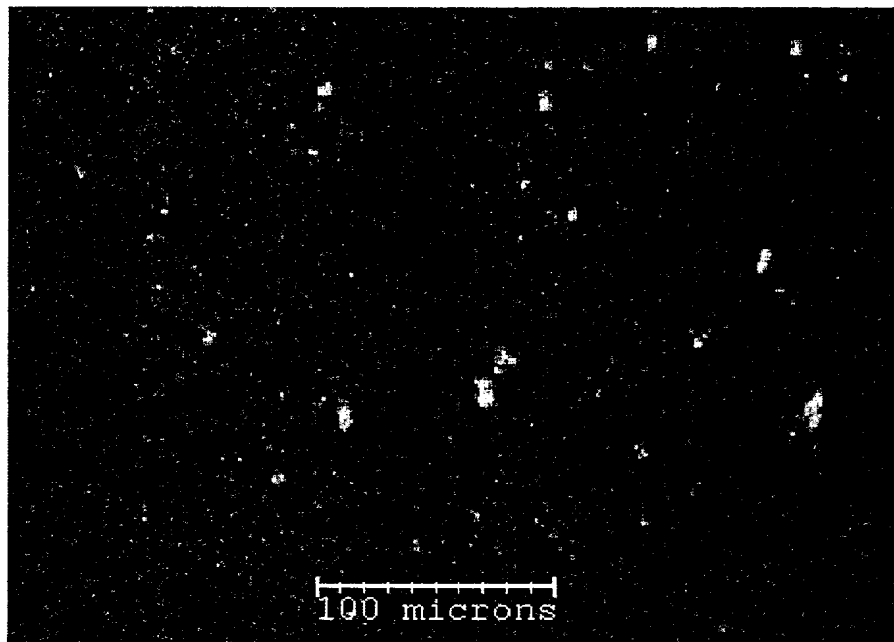
EVA 46: SILICA MAPPING



Si

FIG. 1

EVA 47: SILICA MAPPING



Si

FIG. 2

2 / 3

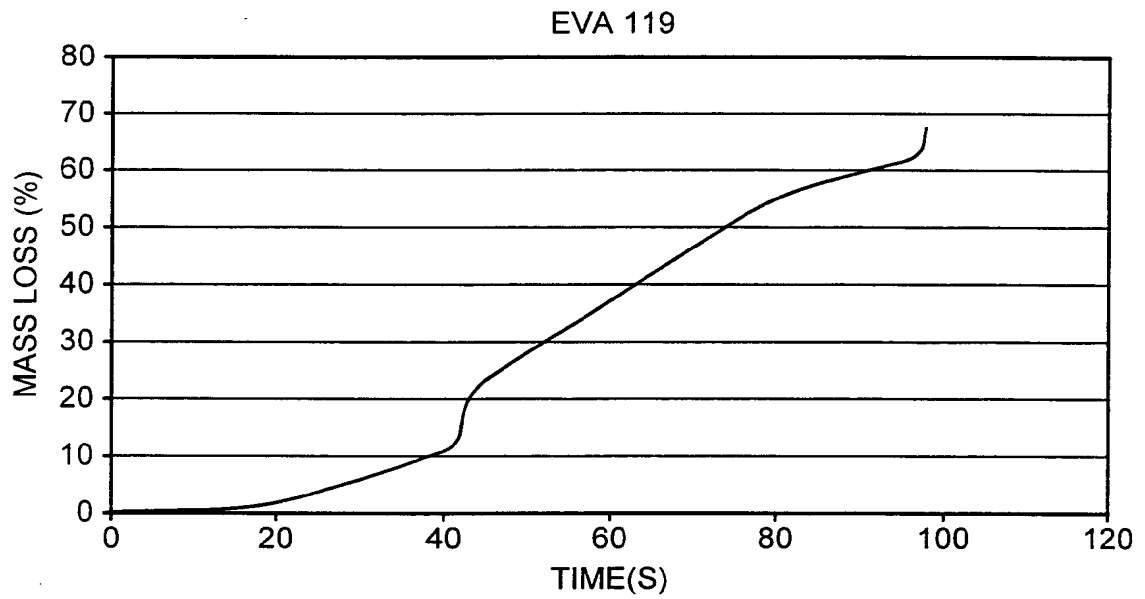


FIG. 3

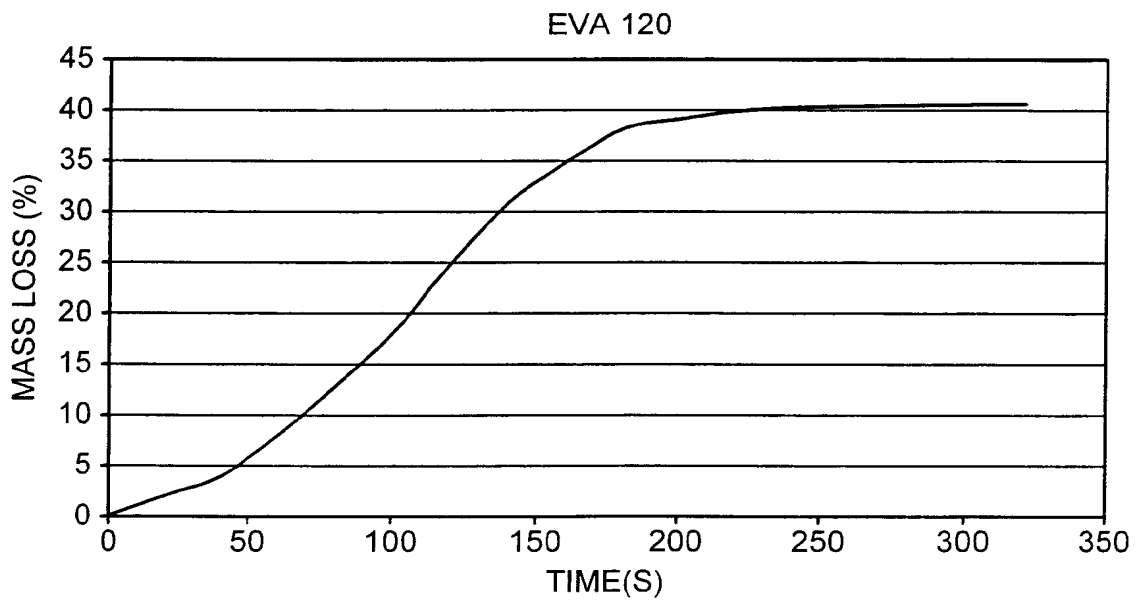


FIG. 4

3 / 3

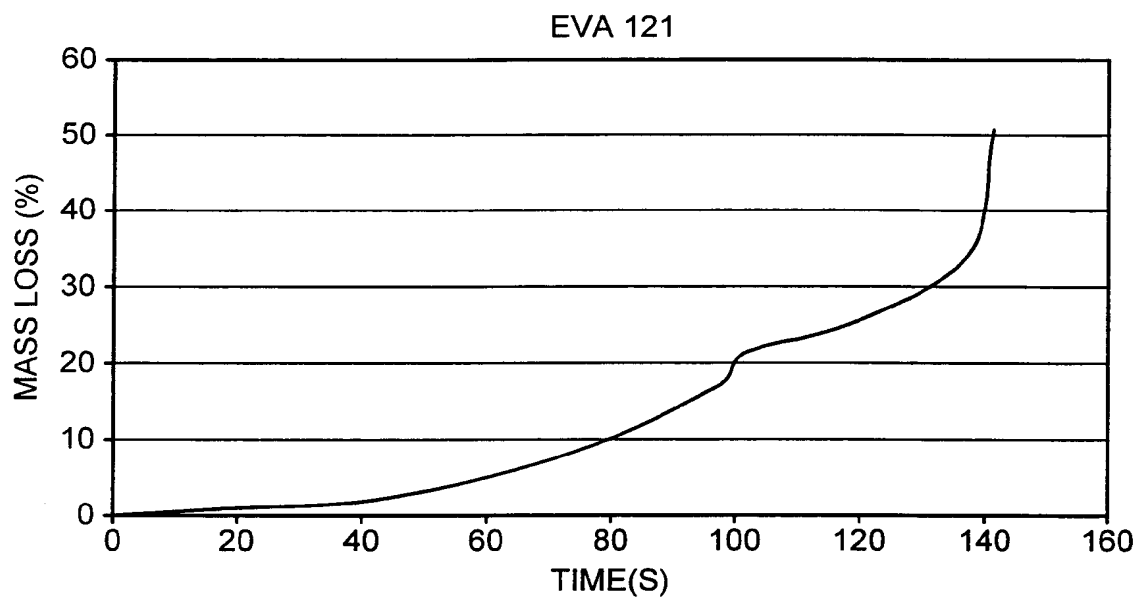


FIG. 5

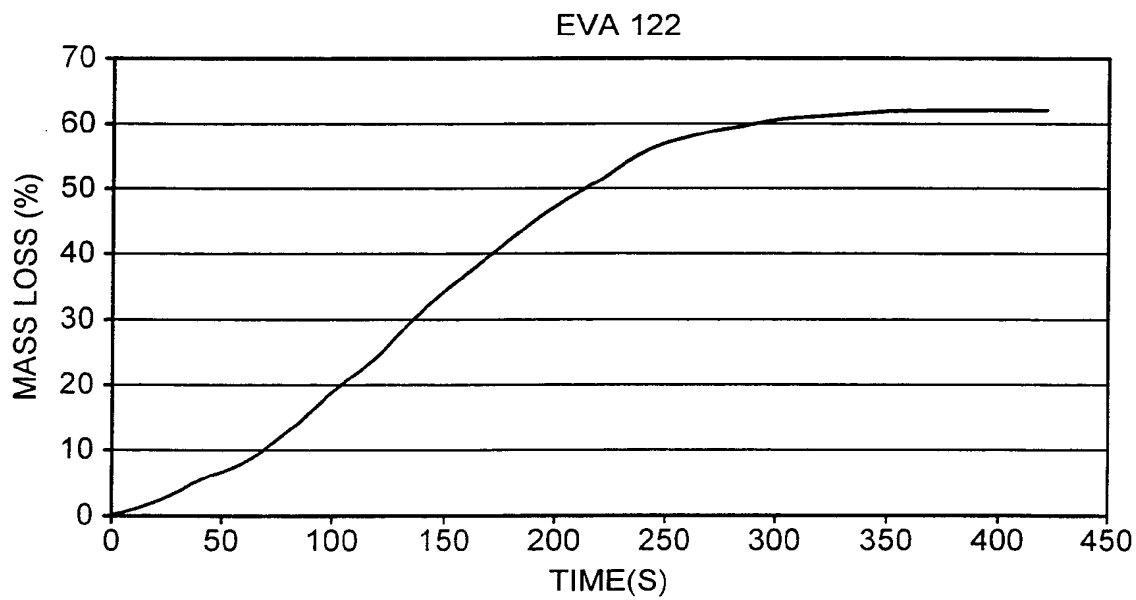


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01652

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K3/34 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 459 472 A (TOYODA CHUO KENKYUSHO KK) 4 December 1991 (1991-12-04) claims 1-11	1-8, 11
A	WO 97 30950 A (DOW CHEMICAL CO ;SOUTHERN CLAY PROD INC (US)) 28 August 1997 (1997-08-28) cited in the application page 10, paragraph 3 -page 11, paragraph 3 example 1 claim 1	1-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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